X-ray photoelectron spectroscopy investigation of the mixed anion GaSb/InAs heterointerface

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X-ray photoelectron spectroscopy has been used to measure levels of anion cross-incorporation and to study interface formation for the mixed anion GaSb/InAs heterojunction. Anion cross-incorporation was measured in 20 Å thick GaSb layers grown on InAs, and 20 Å thick InAs layers grown on GaSb for cracked and uncracked sources. It was found that significantly less anion cross-incorporation occurs in structures grown with cracked sources. Interface formation was investigated by studying Sb soaks of InAs surfaces and As soaks of GaSb surfaces as a function of cracker power and soak time. Exchange of the group V surface atoms was found to be an increasing function of both cracker power and soak time. We find that further optimization of current growth parameters may be possible by modifying the soak time used at interfaces.

I. INTRODUCTION

The mixed anion arsenide/antimonide system has a number of technologically interesting applications, such as InAs/AlSb oscillators operating at frequencies greater than 700 GHz,[1] novel InAs/AlSb/GaSb based[2–4] and InAs/GaSb[5] tunnel structures, and InAs/$Ga_{1-x}In_xSb$ infrared (IR) superlattice (SL) detectors.[6,7] One of the main problems in growing such arsenide/antimonide structures is controlling the structural and chemical properties of the interface. Typically, III–V structures are grown with group V overpressures, since their vapor pressures are much larger than the group III vapor pressures. In growing mixed anion structures, such as in the arsenide/antimonide system, this overflux of the group V element becomes a problem at those interfaces with mixed anions. Specifically, cross-incorporation of the anion species[8] and variation in interface composition have been observed. In IR SL structures, cross-incorporation of the anion species can result in shorter carrier lifetimes and poor quality material, while the interfacial composition affects the type and level of the background doping, and also affects the SL band gap due to changes in the strain configurations at the interface.[9] Also, the interface composition in the InAs/AlSb system affects the carrier mobility, carrier concentration, and the InAs/AlSb valence band offset.[10,11] Thus, it is important to be able to grow arsenide/antimonide structures with no anion cross-incorporation, and with abrupt, composition controllable interfaces.

In this work, we use x-ray photoelectron spectroscopy (XPS) to study the growth of GaSb/InAs structures using molecular-beam epitaxy (MBE). The GaSb/InAs system is amenable to XPS study due to the lack of elements common to both sides of the heterojunction. Also, since we are primarily interested in controlling the growth of mixed anion interfaces, the results from our study should be easily extendible to the growth of any of the arsenide/antimonide structures described above. The XPS experiments consist of studying core-level peak intensities and separations as a function of cracker power and soak time, where a soak consists of exposing an InAs (GaSb) surface to an Sb (As) flux. Heterojunctions, consisting of GaSb-on-InAs and InAs-on-GaSb, are studied. Results from As soaks of GaSb surfaces, and Sb soaks of InAs surfaces which duplicate the soaks used in heterostructure growths are also presented. In addition, time resolved studies of Sb soaks of InAs surfaces are examined. The heterojunction studies show that levels of anion cross-incorporation can vary markedly depending on the cracker power used during growth. In the group V soak experiments, we find that the anion exchange is highly dependent on the cracker power and the soak time.

In Sec. II, we describe the MBE growth and the details of the XPS experiments and data analysis. Section III presents the results from the XPS studies. In Sec. IV, we discuss the XPS results, and in Sec. V we summarize the article.

II. EXPERIMENT AND DATA ANALYSIS

All of the structures studied here were grown in a Perkin–Elmer 430 MBE system equipped with cracked Sb and As sources. Two cracker powers, 80% and 40%, were used to emulate growth systems with and without cracked sources, respectively. We refer to the source fluxes by their primary component; Sb_4 and As_4 (uncracked) at 40% cracker power, and Sb_2 and As_2 (cracked) at 80% cracker power. The structures were grown on a number of different (100) substrates (GaAs,*n*-GaSb,*p*-GaSb), with no variation in results. Samples were grown on thick stress relaxed GaSb buffer layers at a substrate temperature of ~380 °C. Multiple samples grown on the same substrate were separated by buffer layers thick enough to prevent detection of underlying layers with XPS. Details of the growth may be found in Ref. 12.

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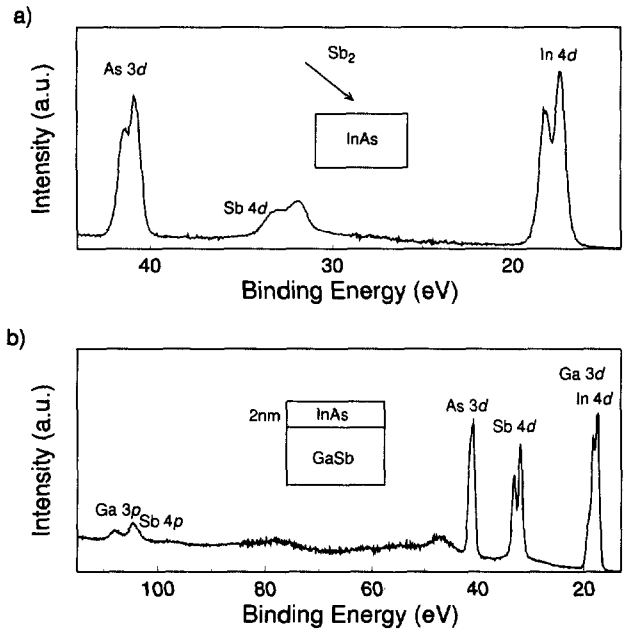

FIG. 1. XPS binding energy spectra of (a) 15 s Sb_2 soak of InAs surface and (b) a 20 Å thick InAs layer grown on GaSb. The sample structures are shown in the insets.

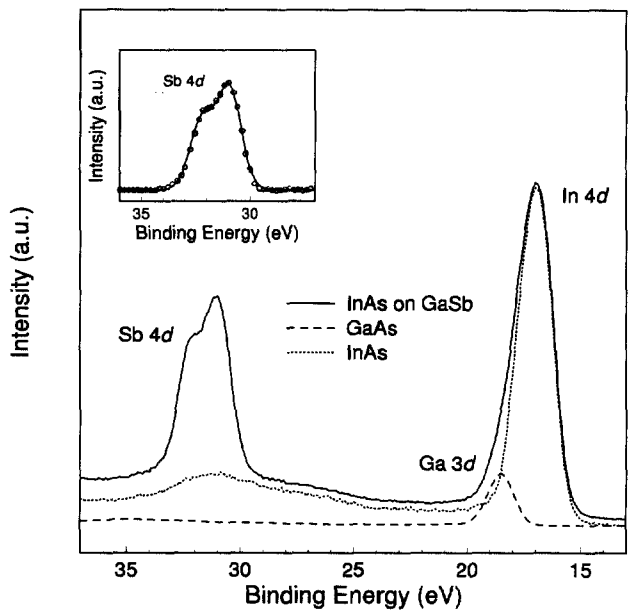

FIG. 2. XPS data analysis of an InAs-on-GaSb sample. Peaks from InAs standards (dotted) and GaAs standards (dashed) are used to remove the In 4*d* and Ga 3*d* loss tails from the Sb 4*d* peak. Inset shows resulting fit of Sb 4*d* peak.

The XPS measurements were obtained using a Perkin–Elmer Model 5100 analysis system with a monochromatic Al $K\alpha$ source ($h\nu = 1486.6$ eV). All of the samples studied were transferred from the growth chamber to the XPS chamber via an ultrahigh vacuum transfer tube. The base pressure in the XPS chamber was typically $\sim 1 \times 10^{-10}$ Torr. Care was taken to ensure that the escape orientation of the photoelectrons remained constant from sample to sample to minimize any electron diffraction effects due to the single crystalline nature of the samples.

Figure 1 shows two sample XPS spectra. Figure 1 (a) shows a spectrum from an InAs epilayer with a 15 s Sb_2 soak, and Fig. 1 (b) shows a spectrum from a thin (nominally 20 Å) layer of InAs on GaSb. This thickness allows adequate detection of photoelectrons from both the GaSb and InAs layers. The data analysis for the Sb soaks of InAs surfaces consisted of isolating the Sb 4*d*, In 4*d*, and As 3*d* core-level peaks, performing an integrated background subtraction, fitting these peaks to Voigt functions, and determining the corresponding integrated intensities, and core-level binding energies. From the peak intensities, we were able to estimate the Sb coverage on InAs. A similar procedure was used for the analysis of the As soaks of GaSb surfaces, except that the As 3*d*, Ga 3*d*, and Sb 4*d* peaks were used. To estimate the group V coverage, we used a simple attenuation model based on published effective photoelectron mean free paths (MFPs).[13–15] Due to the uncertainty in these MFPs, this procedure cannot be used to quote precise compositions; however, comparisons between samples are certainly valid. As mentioned above, it is crucial to device performance to be able to accurately control the interface composition. By studying the surface after the soaks, we are essentially viewing the chemical structure of the interface as it is being formed. This allows us to determine the growth conditions and shuttering sequence required to obtain a particular interface structure. For the heterojunction experiments, the intensities and binding energies of the following peaks are determined: As 3*d*, In 4*d*, Ga 3*d*, Ga 3*p*, and Sb 4*d*. The ratio of As 3*d* to In 4*d* peak intensities are measured and normalized to the As 3*d* to In 4*d* peak intensity ratio for an As terminated (2×4 reconstruction) InAs standard. Similarly, the Ga to Sb peak intensity ratios are normalized to an Sb terminated (1×3 reconstruction) GaSb standard. From the variation in these peak intensity ratios, we are able to estimate relative levels of cross-incorporation as a function of cracker power.

Some care must be taken in the data analysis described above. As seen in Fig. 2, many of the XPS features overlap. In this case, the Ga 3*d* and In 4*d* peaks overlap, and their plasmon loss tails interfere with the Sb 4*d* peak. To isolate the Sb 4*d* peak, we first fit the Ga 3*d* and In 4*d* peaks to peaks shapes obtained from GaSb and InAs standards. Then, using the GaAs and InAs standards, we perform spectrum stripping to remove the Ga 3*d* and In 4*d* loss tails from the Sb 4*d* signal. The inset in Fig. 2 shows the Sb 4*d* peak after background subtraction, and the resulting fitted Voigt functions. In addition to interferences from overlapping features, chemically shifted components must be accounted for. Figure 3 shows the Sb 4*d* signal from a sample consisting of a 15 s Sb_2 soak of an InAs surface. The two spin-split doublets comprising the Sb 4*d* peak were obtained by stripping off the In 4*d* loss tail, subtracting the integrated background function, and fitting the resulting spectra to two Sb 4*d* peaks with their peak shapes constrained to that of Sb 4*d* from a GaSb standard. Only a scale and a binding energy (BE) parameter were allowed

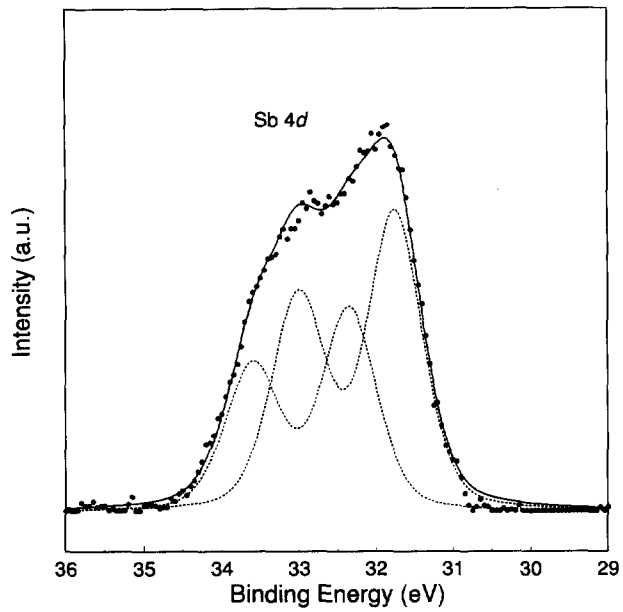

FIG. 3. Sb 4*d* peak from 15 s Sb_2 soak of InAs surface. Data are fitted with two chemically shifted peaks with line shapes constrained to that of Sb 4*d* from bulk GaSb.

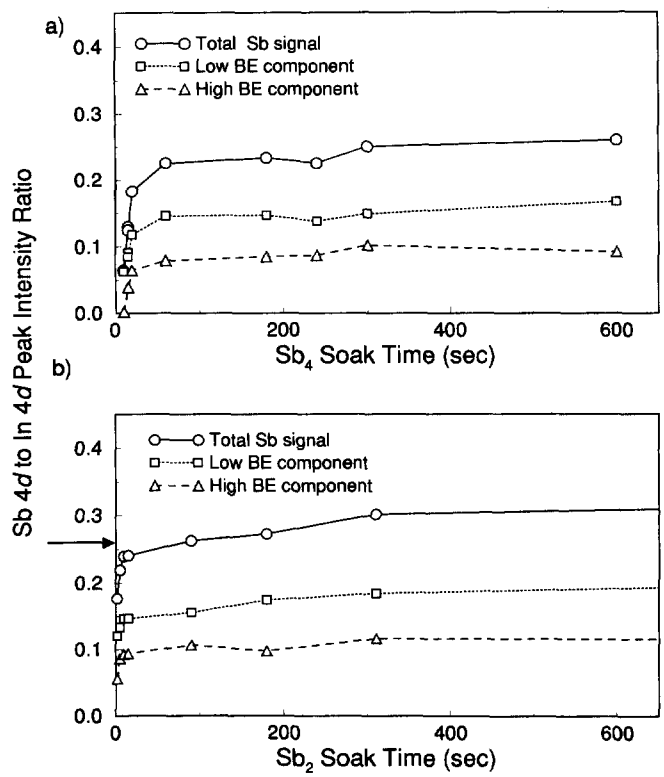

FIG. 4. Sb 4*d* to In 4*d* peak intensity ratio as a function of soak time for (a) uncracked, and (b) cracked Sb sources. Components of the total peak are also shown (dotted and dashed lines). Lines are drawn for visualization purposes only. In plot (b) lines extend to additional data points at 1800 s.

to vary for each of these doublets. Using these techniques, core-level binding energy separations and peak intensities on identical samples were typically reproducible to better than ±0.03 eV and ±5%.

III. RESULTS

The group V soak experiments were done in two parts. In the first experiment, the cracker power and soak time were chosen to duplicate the conditions during growth of actual devices. For the 5 s Sb_2 and Sb_4 soak of an InAs surface, the As to In peak intensity ratio decreased by 18% and 1% relative to bulk InAs. Using an attenuation model, this corresponds to a majority of the terminating As layer being exchanged during the Sb_2 soak, and very minimal exchange during the Sb_4 soak. Given the uncertainty in published MFPs, we can only estimate relative changes in coverage, and cannot quote exact values, For the 5 s As_2 and As_4 soaks of GaSb surfaces, the Sb 4*d* to Ga 3*d* peak intensity ratio decreased by 26% and 7% relative to bulk GaSb. This corresponds to roughly complete exchange of the terminating Sb layer for the As_2 soak and partial exchange for the As_4 soak.

The heterojunction experiments allow us to estimate relative amounts of cross-incorporation. For InAs on GaSb grown with As_2 and Sb_2, the Sb 4*d* to Ga 3*d* peak intensity ratio decreased by 24%, which is consistent with an abrupt interface with minimal cross-incorporation of Sb atoms into the InAs layer. The same structure grown with As_4 instead of As_2 showed a 11% increase in the Sb 4*d* to Ga 3*d* peak intensity ratio relative to bulk GaSb. This increase can be reasonably explained only by an increase in the amount of Sb incorporating into the InAs layer. GaSb on InAs structures grown with cracked and uncracked Sb were also studied. In this case, the As 3*d* to In 4*d* peak area ratio increased for both structures, but increased significantly more (51% versus 16%) for the sample grown with Sb_4. Again, the only reasonable explanation for this difference is more cross As incorporation occurring in samples grown with uncracked sources.

In the second soak experiment, Sb coverage on InAs as a function of both cracker power and soak time was studied. Since the 5 s Sb_2 soak at growth conditions resulted in roughly complete exchange of the As terminated surface, the bulk evaporator temperature was lowered to reduce the total Sb flux impinging on the sample surface by roughly 80%. This increases the exchange time, allowing better time resolution of the exchange process. Figure 4 shows the ratio of the Sb 4*d* to In 4*d* peak intensities as a function of soak time for (a) 40% cracker power, and (b) 80% cracker power. As expected, the Sb coverage increases with time of soak and, at low soak times, is significantly greater for cracked soaks than for uncracked soaks. The features of Fig. 4, and the chemically shifted Sb 4*d* component shown in Fig. 3 are discussed below.

IV. DISCUSSION

As mentioned above, the heterojunction studies showed that more cross-incorporation occurred when using uncracked sources; however, uncertainties in the published electron MFPs and the exact distribution of cross-incorporated anions prevent us from stating absolute in-

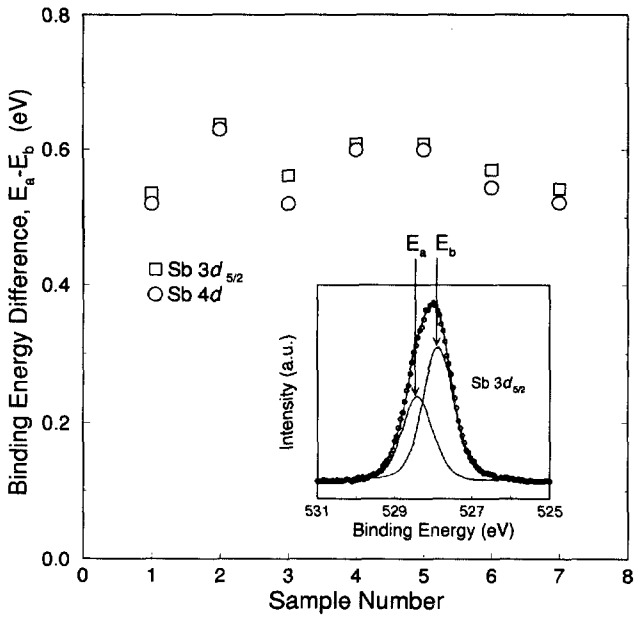

FIG. 5. Energy seperation between the two component peaks for the Sb 3*d* and Sb 4*d* core levels. The same fluctuation in seperation is observed for both peaks. Inset shows components comprising Sb 3*d* peak. Sb 4*d* peak is shown in Fig. 3.

corporation levels. We were unable to fit all of the measured core level ratios using a theoretical sample structure with reasonable layer thicknesses. Typically, the Ga 3*d* to Ga 3*p* peak intensity ratio could only be fit by decreasing the electron MFP for Ga 3*p* photoelectrons below published values. Since the values from Refs. 13–15 are not in agreement, and since none contain experimentally measured electron MFPs for our materials, it is quite possible that the actual Ga 3*p* photoelectron MFP is in fact below these published values. It should be noted that the claim of greater levels of cross-incorporation occurring when using uncracked sources instead of cracked sources is independent of the validity of the published MFPs.

Although we are not able to accurately determine surface coverages in the devicelike group V soak experiments using photoelectron MFPs, we can estimate the surface coverages by studying the time dependent soak experiments. To do this, we need to determine the source of the chemically shifted Sb 4*d* component shown in Fig. 3. A detailed analysis of this peak shows a variation in the magnitude of the chemical shift of more than 0.1 eV. This is a large variation considering that the chemical shift is only ~0.5 eV; however, as can be seen in Fig. 5 analysis of the higher BE Sb $3d_{5/2}$ core level reveals a nearly identical variation in the separation between its constituent peaks. This demonstrates that the variation in peak separation is a real effect and not an artifact of the XPS data acquisition. One possible explanation for the second Sb component might be a surface reconstruction related shift; however, the lack of a shifted component at very low soak times argues against this theory. Another possible explanation for the two Sb components is the formation of metallic Sb islands. If true, then based on the direction of the observed chemical shift, the higher BE Sb peak should be due to the islands.[16] To check this, we measured the BE of metallic Sb 4*d*, from a thin metallic Sb layer grown on InAs. The measured Sb 4*d* BE was less than the BE of the shifted Sb 4*d* peak, which is consistent with the shifted peak being due to metallic Sb islands, since islanding can shift peaks to higher binding energy. Island formation may also explain the variation in the position of the chemically shifted peak, since changes in average island size can cause a change in the magnitude of the chemical shift. In addition, the energy separation between the lower BE Sb 4*d* peak and the In 4*d* peak is stable, making it reasonable to believe that this peak is due to an exchanged layer of Sb bonded to In which should be stable from sample to sample, while the higher BE peak, due to islanding, may vary from sample to sample. Also, referring to Fig. 4, we see that since the low BE Sb peak in both the cracked and uncracked soaks stabilize at roughly the same value, it is quite possible that the steady state value corresponds to exactly 1 monolayer (ML) of Sb atoms exchanging with the As terminated InAs surface. If this is the case, then the coverage obtained with the Sb_2 devicelike soaks is slightly less than 1 ML, as indicated by the arrow in Fig. 4 (b). It should be noted that even if the islanding explanation proposed above is incorrect, the fact that current soaks occur in a region where the coverage is dependent on the time of soak indicates that further optimization of growth parameters may be possible.

V. SUMMARY

In conclusion, we have used XPS to study anion cross-incorporation and interface formation as a function of cracker power and soak time for the mixed anion InAs/GaSb heterostructure. Studies of interface formation revealed that anion exchange occurs more readily when using cracked versus uncracked sources for the soak. In addition, studies of InAs-on-GaSb and GaSb-on-InAs heterostructures showed significantly more anion cross-incorporation when using uncracked sources. Varying the soak time for Sb soaks of InAs surfaces showed a leveling off of the Sb coverage for longer soak times. Based on detailed analysis of the XPS core level peaks, we see evidence for island formation and conclude that the steady-state coverage may correspond to ML exchange of the As terminated surface with Sb, and the formation of metallic Sb islands. Since current soaks used in actual device growth lie in a region where variations in soak time may vary the extent of the group V exchange, further optimization of growth parameters may be obtained by modifying these soak times.

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